12-1987

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Abstract
The effect of the hybridization of 4*f* electrons on La, Ce, and Pr tripositive ions with ligand states or conduction electrons was simulated by reducing the Slater integrals involving the 4*f* electrons by 10% or 20%, depending on whether the integrand involves one or two 4*f* electrons, respectively. The dipole-allowed *4d→4f* spectra were calculated. Observable effects, changes in line energies, and oscillator strengths, were compared with limited data available for ionic and metallic solids containing these lanthanides, and for Ce vapor. Many of the observed changes in the *4d→4f* spectra attributed to hybridization effects are found qualitatively in the calculation.

Keywords
Ames Laboratory, tripositive ions, Slater integrals

Comments
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Effect of hybridization on $4d \rightarrow 4f$ spectra in light lanthanides

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(Received 22 June 1987)

The effect of the hybridization of $4f$ electrons on La, Ce, and Pr tripositive ions with ligand states or conduction electrons was simulated by reducing the Slater integrals involving the $4f$ electrons by 10% or 20%, depending on whether the integrand involves one or two $4f$ electrons, respectively. The dipole-allowed $4d \rightarrow 4f$ spectra were calculated. Observable effects, changes in line energies, and oscillator strengths, were compared with limited data available for ionic and metallic solids containing these lanthanides, and for Ce vapor. Many of the observed changes in the $4d \rightarrow 4f$ spectra attributed to hybridization effects are found qualitatively in the calculation.

INTRODUCTION

The $4d \rightarrow 4f$ transitions in rare-earth ions[1–8] are widely used in the photoelectron spectroscopy of rare-earth metals, and compounds and alloys which contain them, via the technique of resonance photoelectron spectroscopy.[9–11] In such studies, small changes in the "fine structure" below the threshold for continuum transitions occur as the environment of the rare-earth metal changes. Figure 1 gives an example of this for Ce,[12] perhaps the lanthanide most frequently studied. These changes primarily consist of changes in the widths of structures, but peak position and relative strength changes occur also. Similar effects can be brought about by changes in temperature as well.[13] Such changes have been attributed to changes in hybridization of the $4f$ electron(s) in the initial and final states of the transition with other states of the rare-earth ion, e.g., in the difference between γ-Ce and α-Ce metals, or with ligand states, e.g., in the difference between γ-Ce and Ce_2O_3. As far as we are aware, there has been no justification for this, i.e., no demonstration that such hybridization can lead to the changes observed.

The theoretical treatment of these transitions is based on the free tripositive lanthanide ion.[14–17] Basis states constructed from one-electron radial wave functions obtained by solution of the Hartree-Fock equations are subjected to exchange and Coulomb terms in the Hamiltonian, which give rise to large (10 eV or so) multiplet splittings. This was carried out for a number of lanthanides by Fano and co-workers,[14–17] who calculated ground-state ($4d^{10}4f^n$) and excited-state ($4d^9 4f^{n+1}$) energies and wave functions. These initially were used to calculate the positions of all dipole-allowed lines in the spectra. When the calculated radial wave functions were used in the Slater integrals, poor agreement with experiment was obtained. However, when the calculated Slater integrals were reduced 25–33 %, good agreement with experiment resulted; positions and strengths of many lines were given in essential agreement with experiment. The number of "adjustable" parameters is considerably less than the number of experimental features. The reduction of the Slater integrals was later shown to be expected, for it has an effect similar to that of the inclusion of $4d$-shell polarization, which was neglected in the original calculations.[18]

The final states pushed to higher energy autoionize. Dehmer and Starace[17] calculated a linewidth for the strong $^1P_1$ line in La. They obtained a width well below that found in experiment. The experimental line shapes in this region are not as simple as predicted by the mod-

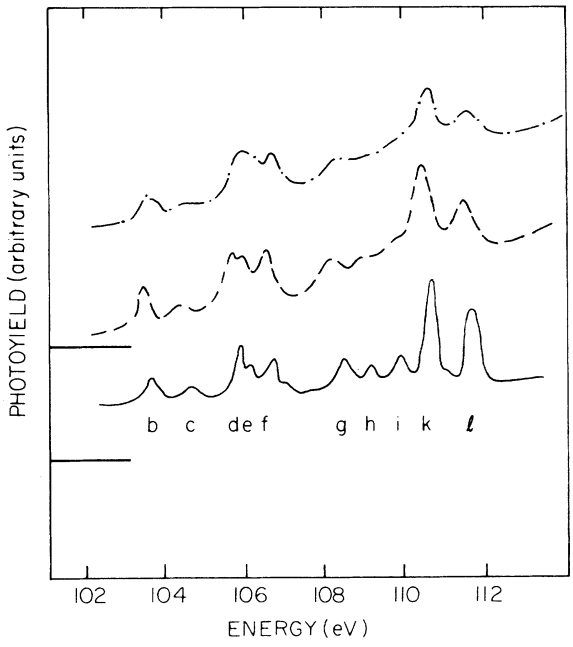

FIG. 1. Low-energy part of the photoyield spectrum for $4d \rightarrow 4f$ transitions in CeF_3 (solid line), γ-Ce (dashed line), and α-Ce (dot-dashed line) (from Ref. 12). The lines are labeled according to the labels in Ref. 7.

el used by Sugar and Dehmer, and they vary from solid to solid, implying departures from the free-ion model. One calculation[19] showed that for this final state in La, the $4f$ radial wave function is considerably more extended than for the states at lower energy. Thus it will be the final state most likely to hybridize with the surrounding electrons.

This treatment, being based on free ions, cannot, of course, directly incorporate the hybridization of lanthanide $4f$ and ligand wave functions. The magnitude of hybridization should be largest for La (in the excited state only), slightly smaller for Ce, then Pr, etc., because of the lanthanide contraction of the $4f$ radius. Photoelectron spectroscopy and a model for its interpretation now widely accepted lead to an estimate for the hybridization of the $4f$ electron in Ce with other states, an estimate of up to about 10% for the $4f$ charge density lost by hybridization.[20,21] In the following we make a quantitative estimate of the effect of this hybridization on the $4d^{10}4f^n \rightarrow 4d^9 4f^{n+1}$ transitions in La, Ce, and Pr, by repeating the calculation of Fano *et al.*, but with reduced Slater integrals to simulate the principal effect of hybridization. If $\psi = a \mid 4f \rangle + b \mid L \rangle$, the ligand component $\mid L \rangle$ will overlap but little with the $4f$ and $4d$ wave functions that cause the large multiplet structure. Thus, reducing those Slater integrals involving one $4f$ state by 10% and those involving two $4f$ states by 20% should provide a qualitative estimate of the effect of hybridization on the spectra. It cannot deal with the broadening of individual spectral features, whose origin is not yet clear, but changes in position and relative strengths should appear.

CALCULATIONS AND RESULTS

The calculations were carried out for free tripositive ions of La, Ce, and Pr using an atomic code developed previously.[22] The Slater integrals given by Sugar were used initially, and the program gave ground-state energies and the energies of all excited states of the $4d^9 4f^{n+1}$ configuration. The oscillator strengths and energies of all dipole-allowed transitions were also calculated. The results differed slightly from those of Sugar because of rounding errors, but that is not important for the purpose at hand. Those Slater integrals that involve one $4f$ electron were then reduced by 10% and those for two $4f$ electrons by 20%, and the program run again. This should simulate a situation in which the $4f$ electrons hybridize. This model is not quantitative. The lanthanide contraction causes the $4f$ states to hybridize less with increasing atomic number, so the reduction in Slater integrals should not be the same for all lanthanides. Also, for one lanthanide all $4f$ states do not have the same radius,[19] so they will not hybridize to the same extent. Moreover, the $4d$ hole in the excited state may reduce the average $4f$ radius some, although the full $Z+1$ approximation will be invalid because of the comparable radii of the two subshells.

La has only three dipole-allowed transitions. Two of them are very weak because they arise from transitions to nominally triplet final states. These are shown on a logarithmic scale in Fig. 2, where it is easy to see that all three lines shift in energy and change strength, but the spectrum does not shift rigidly.

Ce is more complicated. There are 53 dipole-allowed transitions, some of them very weak. We show in Fig. 3 only those with oscillator strengths f (multiplied by degeneracies g) above 0.01. All other allowed transitions contribute negligibly to measured spectra. The spectra

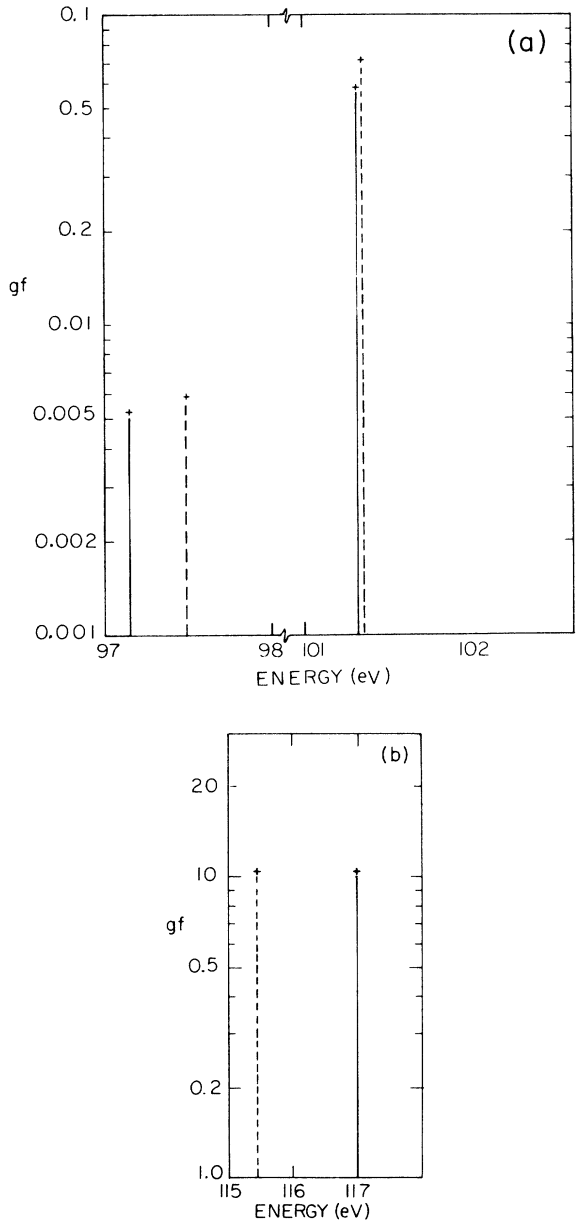

FIG. 2. Calculated $4d \rightarrow 4f$ spectrum for La^{3+}. Solid lines from calculation with Slater integrals used by Sugar (Ref. 16). Dashed lines from calculation with Slater integrals reduced as described in the text. (a) Low-energy region. (b) High-energy region with autoionization not considered. The ordinate is the product of the oscillator strength f and degeneracy g.

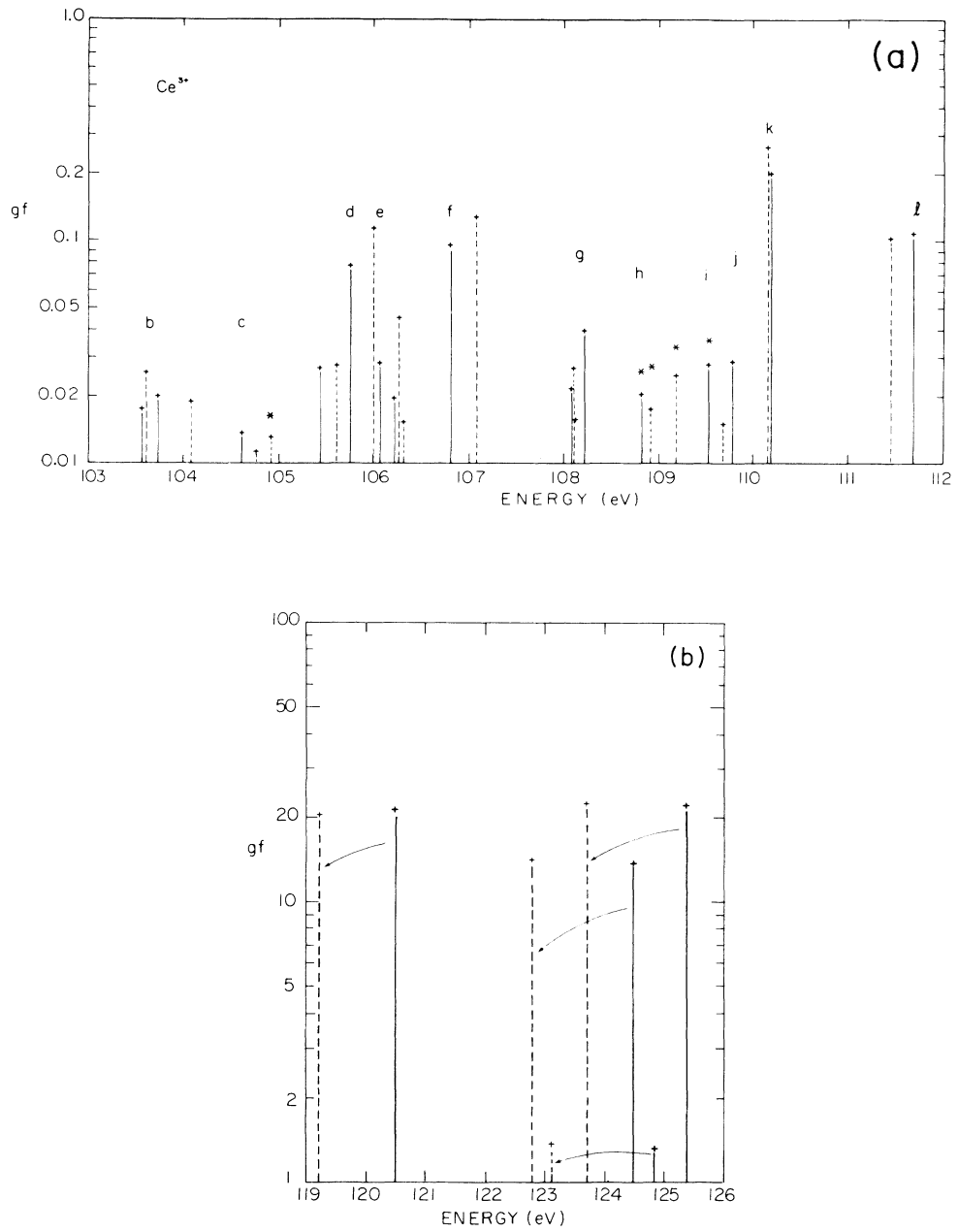

FIG. 3. Calculated $4d \rightarrow 4f$ spectrum for Ce^{3+}. Solid lines from calculation with Slater integrals used by Sugar (Ref. 16). Dashed lines from calculation with Slater integrals reduced as described in the text. Line labels from experimental spectra of Ref. 7. (a) Low-energy region. (b) High-energy region with autoionization not considered.

are shown for the two sets of Slater parameters. A few of the lines change dramatically, those marked with an asterisk. Such lines in the original spectrum weaken below the threshold of the plot when the Slater integrals are changed, and the new lines so marked grow from below threshold as the Slater integrals change. All the other lines shift some and change strength, but not so much. There is no rigid shift, nor monotonic change in strength, for the effect of the change in Slater integrals is complex, as levels shift and parentages change.

Pr is still more complicated, with 144 dipole-allowed transitions. Figure 4 shows a plot of those lines with strengths above 0.01, as for Ce in Fig. 3. The effects are much the same, except that at higher energies, the shifts in the positions of the lines are greater, up to almost 2 eV. (As mentioned above, the fractional reduction in the

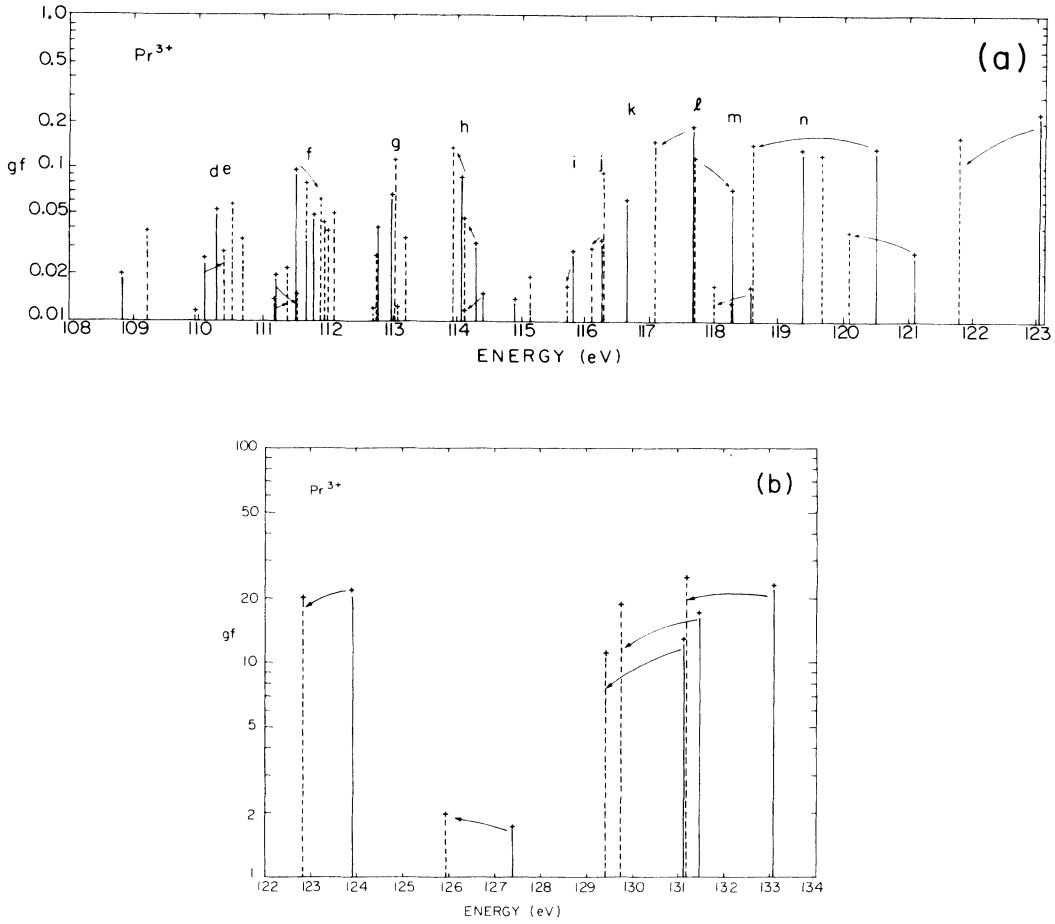

FIG. 4. Calculated $4d \rightarrow 4f$ spectrum for Pr^{3+}. Solid lines from calculation with Slater integrals used by Sugar (Ref. 16). Dashed lines from calculation with Slater integrals reduced as described in the text. Line labels from experimental spectra of Ref. 28. (a) Lower-energy region. (b) Higher-energy region without consideration of autoionization.

Slater integrals should get smaller with increasing lanthanide atomic number.)

DISCUSSION

Because the shifts are often very small, it is difficult to compare meaningfully data taken by different investigators on different instruments. It should be possible to compare line separations in complex spectra taken on different monochromators even when the absolute energy calibrations differ, but the amount of data available is not great, the largest amount being available for Ce and its compounds. The larger shifts at the high-energy end of the Ce and Pr spectra will also be difficult to study because the spectral lines are greatly broadened by autoionization. The shifts in the central part of the Pr spectrum are large enough that a meaningful comparison of data taken on different monochromators could be made.

For La, there are only three lines and one is extremely weak. Rabe[4] measured absorption spectra for La, LaF_3, $LaCl_3$, $LaBr_3$, and LaI_3. The peak positions of the $^3D_1$ peak ranged from 101.63 eV for the iodide to 101.78 eV for the fluoride, with an estimated uncertainty of ± 0.03 eV. The weaker $^3P_1$ peak ranges from 97.29 eV in the metal to 97.39 eV in the fluoride, a smaller spread in energy, despite the larger shift for this line shown in Fig. 1. No systematic trend can be identified in the data.

Miyahara *et al.*[23] also measured La and LaF_3. They fit both peaks with a Fano[24] line shape, finding a large asymmetry parameter q, indicating a slightly asymmetric line shape, and a width parameter Γ that was about 50% larger for the $^3D_1$ line in the metal than for that line in the fluoride, indicating better overlap of the La $4f$ states with La $5d$ states in the metal. No quantitative conclusions about hybridization can be drawn from this work. It shows, however, that the finite widths of the "lines" do not arise only from the lifetime of the final states. There is a contribution from interaction with a background continuum.

The temperature dependence of the two stronger lines in the La $4d \rightarrow 4f$ spectrum has been measured in LaF_3.[13] The strongest line is complicated by autoionization effects, but the line at 101.3 eV [Fig. 2(a)] is simple. An increased temperature causes it to broaden, and to shift slightly to lower energy. The major effect is the increased broadening. An increase in temperature will increase the amplitude of lattice vibrations and increase the average lattice parameter. The electrons respond to the instantaneous position of the atoms, so the vibrating lattice causes a periodic hybridization which leads to the broadening observed. Thermal expansion leads to reduced hybridization with fluoride ligands because of poorer overlap. This should lead to a slight red shift [Fig. 2(a)], in agreement with the observed small shift.

Figure 5 shows the absorption spectrum of Ce vapor and metallic fcc (γ) Ce. There is also a calculated spectrum (dashed lines) similar to the one reported in Fig. 3, which was then broadened for comparison with experiment. The peaks in the two experimental spectra are labeled with corresponding upper and lower case letters. Upon going from the vapor to the solid, peak *b* shifts to higher energy, peak *c* grows stronger, peaks *d*, *e*, and *f* shift to higher energy, peaks *g* and *h* shift to higher energy, and *g* grows in strength with respect to *h*. Peak *k* does not shift and peak *l* shifts to lower energy. In Fig. 3 we have used the same labels as in Fig. 5, and we can see that nearly all these trends are in the calculation; going from the solid lines to the dashed lines represents going from no hybridization with other states to some hybridization, i.e., from atom to solid.

Figure 1 shows photoyield spectra for CeF_3, γ-Ce, and α-Ce. The latter two are both fcc metals, but α-Ce has 15% less volume per atom than γ-Ce, so more hybridization is expected. Estimates of hybridization can be made from various experimental data, although the result may depend on the data used. By all measures α-Ce always has more hybridization than γ-Ce, values of 12% (α) and 2% (γ) for the loss of $4f$ charge density resulting when several types of spectroscopic data are used.[25,26] We can see the same trends in Fig. 1 as in Fig. 5. CeF_3 apparently has less hybridization, γ-Ce more, and α-Ce still more.

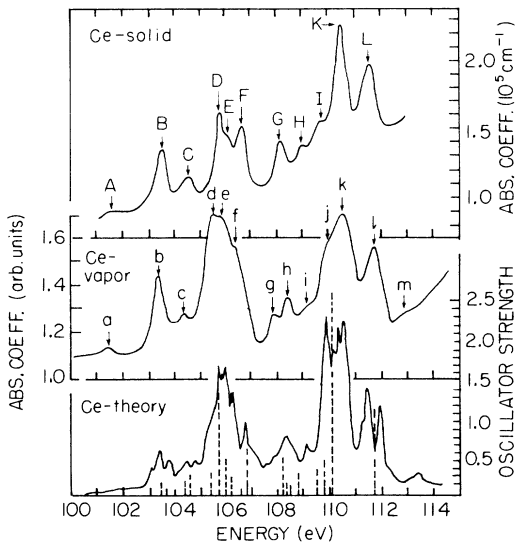

FIG. 5. Experimental absorption spectra for Ce. Upper panel: Ce metal (γ-Ce). Center panel: Ce vapor. The lower panel is from a calculation similar to the one by Sugar and reported here (dashed lines) which was then broadened for comparison with experiment (solid line) (from Ref. 7).

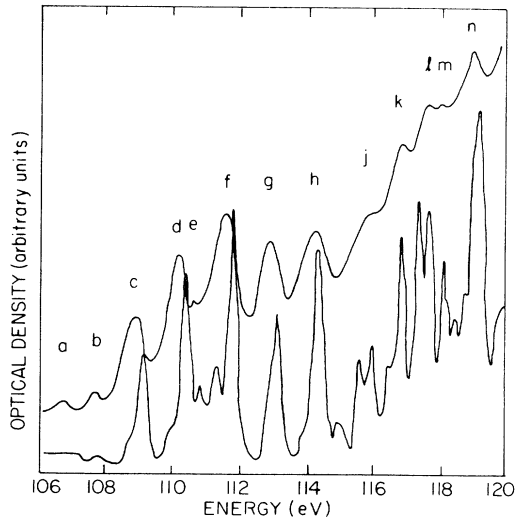

FIG. 6. Experimental absorption spectra of PrF_3 (lower spectrum, from Ref. 27) and metallic Pr (upper spectrum, from Ref. 28). The spectra have not been shifted with respect to one another.

There are fewer data for Pr. In particular, there are no spectra for the vapor. We can compare the spectrum of PrF_3 (Ref. 27) with that of Pr metal.[28] These are shown in Fig. 6. This comparison is difficult, for there could be a shift in energy scale because of the use of different monochromators. The separations of the lines should be independent of such overall shifts, however. The spectra are labeled in Fig. 6 and in Fig. 4 with letters assigned to peaks in the spectrum of the metal. (Peak *c* is not given well by this calculation or by earlier atomic calculations.) Peaks *c*–*g* appear at lower energy in the metal compared to those in the trifluoride. Assuming the metal has more hybridization than the trifluoride, these peaks should shift to higher energy by some 0.3 to 0.4 eV in the metal, assuming a loss of 10% of the charge density per $4f$ electron upon hybridization. That they do not could arise from the relative shift of the two spectra due to monochromator calibration. Peak *h* should shift less, some 0.1 eV, and the peaks at higher energy should shift in the other direction, i.e., to lower energy. However, these shifts should not appear in the spectrum as simple shifts. The original peak *k* vanishes, and is replaced by a new peak 0.4 eV toward higher energy, which actually is peak *l* shifted to lower energy by about 0.6 eV. Peak *m* shifts into the original positions of peak *l*. Comparison of Pr with PrF_3 is only qualitative, at best, for the effects of hybridization calculated here are probably too large.

SUMMARY

The calculations reproduce qualitatively some of the larger shifts and line strength changes observed in light lanthanide $4d \rightarrow 4f$ spectra when the environment of the lanthanide ion is changed, although these are small effects. The largest experimental effect of hybridization, the broadening of the spectra, also can be addressed qualitatively, although good understanding of the broadening mechanism is lacking.[13] The magnitude of the localized $4f$ charge lost by hybridization was fixed to be close to that found for α-Ce, and that value used for both the ground and all excited states of La, Ce, and Pr. These simplifications could be removed in future calculations, but the data set for a more quantitative comparison probably is inadequate.

ACKNOWLEDGMENTS

The Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This work was supported by the Director for Energy Research, Office of Basic Energy Sciences. The work was also supported by the U.S. Department of Energy through Los Alamos National Laboratory under Contract No. W-7405-Eng-36 with the University of California.

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